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OBTAINING HEATPROOF COATINGS ON FIRECLAY REFRACTORIES BY SHS

B. B. Khina,[1] A. T. Volochko,[1] and A. A. Zhukova[1]

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The possibility of obtaining heatproof coatings on fireclay refractories by self-propagating high-temperature synthesis in the system $MgO – SiO_2 – Al$ using as the binder liquid sodium glass with the additives sodium tripolyphosphate and titanium dioxide, the latter activating the SHS process, is investigate. The optimal composition is determined and the physical-mechanical properties and the macro- and microstructure of the coatings are investigated.

Key words: self-propagating high-temperature synthesis, heatproof coating, spinel, mullite, physical-mechanical properties, macro- and microstructure.

Protective heatproof coatings and methods of synthesizing them are chosen on the basis of certain criteria, among which are, for example, good adhesion of the coating to the refractory, closeness of the CLTEs of the coating and the base, and others.

In the last ten years the energy-efficient method of self-propagating high-temperature synthesis (SHS), discovered in 1967 by A. G. Merzhanov and his colleagues, has been used to obtain ceramic refractories and protective coatings on steel [1]. SHS is an intense exothermal interaction of the components in the condensed phase that propagates along a reaction mix similarly to a wave of combustion. The method is characterized by low energy consumption, simple equipment, high speed of the process, high productivity, purity of the products, possibility of synthesizing ceramics with different composition and function, as well as mechanisms of phase and structure formation in the final product which are unusual from the stand point of conventional materials engineering. The exothermal interaction during SHS can proceed in the form of a wave of combustion (classical SHS) and in a fast volume reaction regime (thermal explosion) [1].

The SHS method has been used to synthesize refractories in the system $MgO – MgAl_2O_4$ [2], masonry mortar in the system $Al – Fe_2O_3$ – chromite ore [3], materials based on aluminomagnesia and chromomagnesia spinel [4, 5], the refractory system $SiC – Al_2O_3$ [6], and materials based on mullite [7]. The SHS method is also convenient to use for producing single refractories, for example, high-temperature articles and various coats, coatings, and solutions.

The objective of the present work is to synthesize by the SHS method heatproof coatings on fireclay refractories, used as linings for tanks in heating units, for example, for melting aluminum. The system $MgO – SiO_2 – Al$ was chosen to obtain refractory and chemically stable phases — aluminomagnesia spinel and mullite.

Secondary resources — shards of magnesite brick (MgO) (TU 32-34-032–94), silicon dioxide SiO_2 (grade B quartz dust) with particle size less than 315 μm and PAP-2 (GOST 5494–95) aluminum powder — were used as the component of the reaction mixture. The source heat release, supporting the flow of the SHS process in this system, must be a reaction of aluminothermic reduction of silicon oxide.

STUDY PROCEDURE

The system $MgO – SiO_2 – Al$ was investigated to obtain protective heatproof coatings based on a spinel phase and aluminosilicate. Silicon dioxide SiO_2 and aluminum powder served as exothermal reagents, magnesium oxide MgO served as the filler and liquid sodium glass ($Na_2O \cdot nSiO_2 \cdot mH_2O$) with the additive sodium tripolyphosphate ($Na_5P_3O_{10}$)

[1] State Scientific Institution “Physical-Technical Institute of the National Academy of Sciences of Belarus, Minsk, Belarus.

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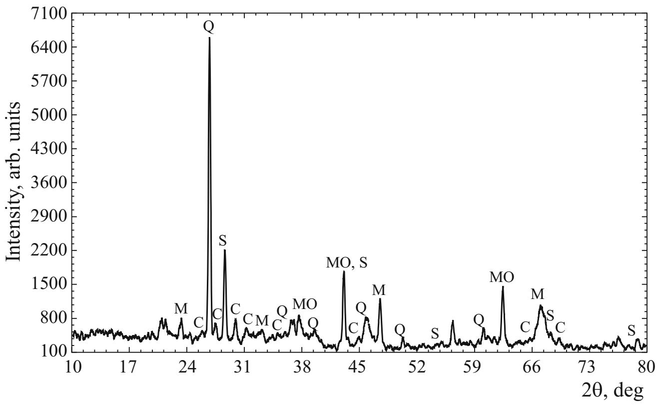

Fig. 1. X-ray phase analysis of the SHS coatings obtained: C) corundum Al_2O_3; MO) magnesium oxide MgO; Q) quartz SiO_2; M) mullite $3Al_2O_3 \cdot 2SiO_2$; S) spinel $MgAl_2O_4$.

served as the binder. For chemical activation of the SHS process, titanium dioxide (TiO_2) was introduced as an additive.

The content by weight of the components in the mix was varied in the following ranges: MgO — 20 – 50%, SiO_2 — 10 – 60%, Al — 20 – 40%.

The components of the system were carefully mixed to obtain the initial mix. Next the binder (liquid sodium glass $Na_2O \cdot nSiO_2 \cdot mH_2O$ (GOST 13078–81)) was introduced with constant mixing until a sour cream like paste was obtained. The paste was deposited on the surface of 32 × 39 mm aluminosilicate tiles. The coated samples were subjected to heat-treatment, which included drying for 16 h at room temperature, 3 h at 100°C, and 3 h at 200°C to remove the chemically bound water molecules. Next the samples were placed in a SNOL-30/1100 thermal furnace and the SHS reaction was initiated by heating the samples to 1000°C. The total time that the samples spent in the furnace at the indicated temperature was 1 h. Such a long soaking time is necessary for completion of all processes resulting in the formation of the final structure and a phase composition of the coating after passage of the SHS wave.

X-ray phase analysis (XPA) of the SHS coatings obtained was conducted with a DRON-3 diffractometer using CuK_α radiation. The x-ray diffraction patterns were interpreted using the Match program [8] and the ASTM card file [9].

The morphology of the surface and microstructure of the SHS coatings were studied with an MIKRO-2000 optical microscope (the concern PLANAR, Belarus) and a Philips SEM 515 scanning microscope.

The adhesion strength was determined according to GOST 28574–90 [10] by detaching a steel cylinder which was attached with epoxy resin to the surface of the protective coating. The heat-tolerance was evaluated by thermal cycling in the following regime: heating of the samples to 1000°C, soaking for 1 h, quenching in water. The number of cycles to failure is an indicator of the heat-tolerance of the coating.

RESULTS AND DISCUSSION

SHS processes in multicomponent systems are complicated [11] and proceed in several successive and parallel stages, which include evaporation of volatile impurities, a change in the aggregate state of one or several initial components (melting) and gas-transport processes (in the heating zone of the SHS wave), formation of grains of intermediate and final phases with respect to exothermal reactions with participation of one- or multicomponent melts (in the zone of the thermal reaction), and final structure formation and partial sintering of the products of heterogeneous interaction in the burn-down zone of the SHS wave [1, 12].

The appearance and propagation of the SHS wave in the layer of reagents deposited on a fireclay substrate was observed visually with the furnace door open. When the furnace was opened the temperature of the sample with the SHS coating decreased because of heat losses, which resulted in a considerable error in temperature measurements performed in the SHS wave using a radiation pyrometer. For this reason, the maximum (neglecting heat losses into the fireclay substrate and the surrounding medium) temperature of SHS was estimated by thermodynamic modeling (TM) using the ASTRA-4 program [13] and the procedure of [14], including repeated calculations in the adiabatic regime with insertion into the thermodynamic database of ASTRA-4 the substances which are missing (complex oxides) and can be formed from the reagents. According to the TM data, the adiabatic temperature of SHS in this system is about 1600 K, which is lower than the melting points of the initial oxides (MgO and SiO_2).

According to the data obtained from x-ray phase analysis (Fig. 1) the final products of synthesis contain the following: mullite $3Al_2O_3 \cdot 2SiO_2$, the aluminomagnesia spinel $MgAl_2O_4$, corundum Al_2O_3, magnesium silicate $MgSiO_3$, and small quantities of unreacted magnesium and silicon oxides.

Synthesis of the mullite and spinel phases in the system under consideration occurs in several stages. The first stage is reduction of silicon from silica by aluminum, which occurs with release of a large quantity of heat:

$$4Al + 3SiO_2 = 2Al_2O_3 + 3Si + Q, \qquad (1)$$

$Q \approx \Delta H^0_{298} = -711$ kJ/mole, where Q is the heat effect, ΔH^0_{298} is the change of the enthalpy of the reaction (1) under standard thermodynamic conditions. The reaction (1) starts at 600°C after aluminum melts.

At the second stage of synthesis at high temperature (in the burn-down zone) spinel and mullite form from the solid oxides according to the following gross reactions:

$$Al_2O_3 + MgO = MgAl_2O_4; \qquad (2)$$

$$3Al_2O_3 + 2SiO_2 = 3Al_2O_3 \cdot 2SiO_2. \qquad (3)$$

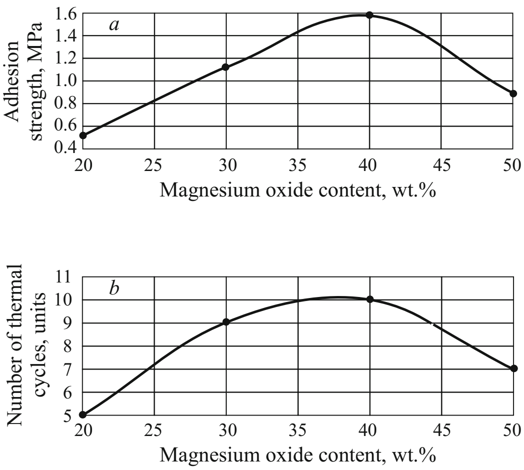

Fig. 2. Physical-mechanical properties of coatings: *a*) adhesion strength of coating; *b*) heat tolerance of coating.

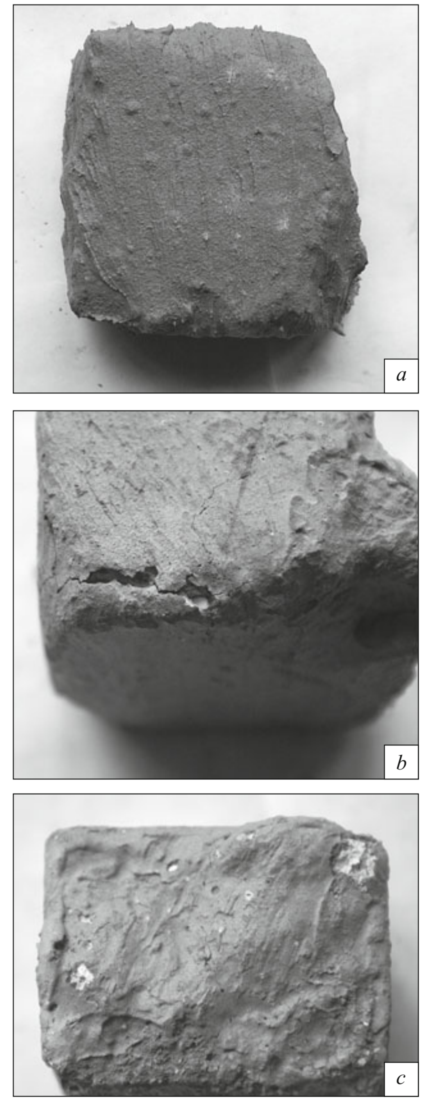

Fig. 3. SHS coating before and after thermal cycling: *a*) no thermal cycling; *b*) 10 heat cycles; *c*) 12 heat cycles.

The reaction (2) is accompanied by negligible heat release: $\Delta H^0_{298} = -22.2$ kJ/mole, and the reaction (3) under standard conditions is slightly endothermal: $\Delta H^0_{298} =$ 29.7 kJ/mole [15]. Most likely, the reaction (3) proceeds in the burn-down zone of the SHS wave and during further soaking of the sample, on which the coating has formed, in the furnace at 1000°C. According to XPA data, after SHS and subsequent calcination in the furnace for 1 h elementary silicon completely vanishes in the products of synthesis and the fraction of unbound aluminum oxide decreases. According to [11] when aluminum oxide interacts with liquid silicon, which is formed in this system according to the reaction (1), kyanite $Al_2O_3 \cdot SiO_2$ can form. According to the XPA results, this compound is absent in the final products. According to [16] mullite formation can proceed at 900°C, while according to the data of [17] kyanite decomposes at temperature above 1250°C with mullite being formed according to the gross reaction

$$Al_2O_3 \cdot SiO_2 = 3Al_2O_3 \cdot 2SiO_2 + 2SiO_2. \quad (4)$$

Thus, a possible primary product of the interaction in an SHS wave (kyanite) is converted into mullite. This agrees with the general principles of the theory of SHS processes [1], according to which the primary product of high-temperature interaction, whose formation is related with the least kinetic difficulties, can exist only a short time in a narrow reaction zone and convert into the final phase (in this case mullite) in the burn-down zone.

The physical-mechanical properties of the SHS coatings obtained were studied in order to optimize the composition of the mix.

The mass content of the components in the mix was varied within the following limits: MgO — 20 – 50%; SiO_2 — 10 – 60%; Al — 20 – 40%. The best values of the adhesion strength (1.59 MPa) were found for the composition 40% MgO – 30% SiO_2 – 30% Al (Fig. 2*a*). This same composition of the SHS coating manifested adequate stability with 10 thermal cycles (Fig. 2*b*). The macrostructure of the fireclay sample with a coating is shown in Fig. 3. It is evident that for the indicated number of thermal cycles only the fireclay refractory itself decomposes. The formation of chips, cracks, pores, color change as well as brittleness and poor adhesion were observed only when the number of thermal cycles was increased to 12.

The microstructure studies showed that the bonding between the SHS coating and the substrate is formed by penetration of the initial mixture into the pores followed by an interaction between the components of the system as the SHS wave passes with formation of the ceramic material (Fig. 4*a*). The porous structure of the coatings (Fig. 4*b*) is related with the presence of the initial porosity of the reaction mix, gas release during high-temperature synthesis, and

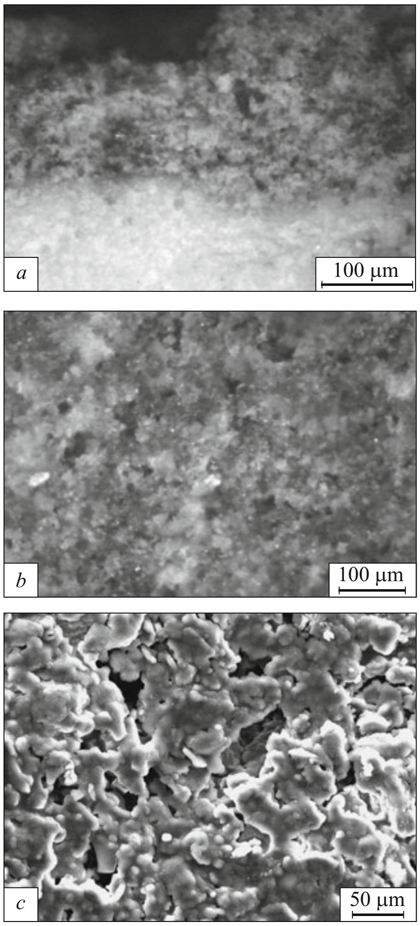

Fig. 4. Structure of SHS coating: *a*) SHS coating – fireclay boundary; *b*) microstructure of SHS coating (optical microscope); *c*) microstructure of SHS coating (scanning electron microscope).

volume changes accompanying phase and structural transformations in an SHS wave and during subsequent cooling. Most of the porosity is blind; the pores are 15 – 30 μm in size and have a nonisometric shape (Fig. 4*c*). The crystalline structure is represented by grains of different size and shape which have grown together, which is related with the partial sintering of the products of synthesis in the burn down zone and with subsequent soaking in a furnace.

CONCLUSIONS

A new composition of heatproof coatings on fireclay refractories has been developed. It consists of a reaction mixture, an activating additive, and a modified binder. Compositions of the system $MgO – SiO_2 – Al$ are used as the SHS mixture and liquid sodium glass with the addition of sodium tripolyphosphate is used as a binder. Titanium dioxide is also added to the mix as an activating additive. The SHS process flow in this system promotes the formation of a protective coating with blind porosity, consisting of chemically inert refractory phases: aluminomagnesia spinel, mullite, corundum, and magnesium silicate. The SHS coating is characterized by high performance properties: high adhesion strength 0.5 – 1.59 MPa and heat tolerance 8 – 10 cycles.

The coatings obtained can be used to protect fireclay refractories from heat shocks in the heating and melting units of production plants.

REFERENCES

1. A. G. Merzhanov and A. S. Mukas'yan, *Solid Flame Combustion* [in Russian], Torus Press, Moscow (2007).
2. G. Xanthopoulou and G. Vekinis, "$MgO/MgAl_2O_4$ refractories by SHS," *Int. J. SHS*, **11**(1), 117 – 129 (2002).
3. G. I. Ksandopulo, M. B. Ismailov, B. N. Sambaev, et al., *RF Inventor's Certificate No. 1717586, Refractory Solution for Periclase-Chromite Masonry Articles* [in Russian] (1992).
4. E. Kh. Baimukhamedov, G. G. Gladun, and A. A. Shirinkhanov, "Self-propagating high-temperature synthesis of high-temperature light-weight refractories," *Inzh.-Fiz. Zh.*, **65**(4), 490 – 491 (1993).
5. K. B. Podbolotov and E. M. Dyatlova, "Phase- and structure-formation during self-propagating high-temperature synthesis in the system $Al – MgCO_3 – SiO_2 – C$," *Steklo Keram.*, No. 9, 29 – 33 (2009); K. B. Podbolotov and E. M. Dyatlova, "Phase- and structure-formation during self-propagating high-temperature synthesis in the system $Al – MgCO_3 – SiO_2 – C$," *Glass Ceram.*, **66**(9 – 10), 332 – 336 (2009).
6. B. B. Khina, E. M. Dyatlova, V. V. Sarantsev, et al., "Use of self-propagating high-temperature synthesis to obtain refractory materials and articles based on SiC and Al_2O_3," *Ogneup. Tekh. Keram.*, No. 10, 2 – 13 (2006).
7. A. Esharghawi, C. Penot, and F. Nardou, "Elaboration of porous mullite-based materials via SHS reaction," *Ceram. Int.*, **36**(1), 231 – 239 (2010).
8. *Match! Phase Identification from Powder Diffraction*, URL: http://www.crystalimpact.com/match/
9. *Powder Diffraction File of the International Center for Diffraction Data, PDF*, Philadelphia (1996).
10. *GOST 28574–90. Protection from Corrosion in Construction. Concrete and Reinforced Concrete Construction Buildings. Methods for Testing Adhesion of Protective Coatings* [in Russian], Standartinform, Moscow (2005).
11. I. A. Karpukhin, V. S. Vladimirov, and S. E. Moizis, "Some particulars of phase and structure formation in refractory SHS materials," *Novye Ogneupory*, No. 8, 33 – 36 (2005).
12. B. B. Khina, *Combustion Synthesis of Advanced Materials*, Nova Science Publishers, New York (2010).
13. N. A. Vatolin, G. K. Moiseev, and B. G. Trusov, *Thermodynamic Modeling in High-Temperature Inorganic Materials* [in Russian], Metallurgiya, Moscow (1994).
14. B. B. Khina, A. F. Il'yushchenko, and A. V. Belyaev, "Thermodynamic modeling of a multicomponent powder SHS system," *Poroshk. Metall.*, No. 26, 35 – 42 (2003).
15. M. Binnewies and E. Milke, *Thermochemical Data of Elements and Compounds*, Wiley-VCH, Weinheim (2002).
16. P. P. Budnikov and A. M. Gistling, *Reactions in Mixture of Solid Materials* [in Russian], Stroiizdat, Moscow (1965).
17. H. Jamirson, H. Dixen, and D. Brown, "Kyanite — mineral for regulating the expansion of high-alumina monolithic refractories," *Novye Ogneupory*, No. 8, 10 – 18 (2003).